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Code: 343-53580

## JAPANESE PATENT OFFICE

## PATENT JOURNAL

KOKAI PATENT APPLICATION NO. SHO 56[1981]-118267

Int. Cl. <sup>3</sup> :	H 01 M 4/62
Sequence No. for Office Use:	6821-5H
Application No.:	Sho 55[1980]-20920
Application Date:	February 20, 1980
Publication Date:	September 17, 1981
No. of Inventions:	1 (Total of 2 pages)
Examination Request:	Not requested

## DRY-CELL BATTERIES

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[There are no amendments to this patent]

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Claim

In a dry-cell battery using manganese dioxide as a positive electrode material, zinc as a negative electrode material, and zinc chloride or ammonium chloride as an electrolyte, expanded graphite is used in part or wholly as a conductivity-enhancing additive in the positive electrode mix.

Detailed explanation of the invention

The present invention relates to an improvement with dry-cell batteries, and it aims to furnish dry-cell batteries of excellent discharge performance.

In dry-cell batteries such as cylindrical dry-cell batteries, laminar dry-cell batteries, and thin film type laminar dry-cell batteries, acetylene black is used as a conductivity-enhancing additive in positive electrode mixes. The acetylene black has the advantages of low electrical resistance and [the ability to] hold a large amount of electrolyte due to its porous structure; but when acetylene black is wetted with a manganese dioxide-admixed electrolyte and shaped to a desired positive electrode mix form it can not be shaped unless it is wetted with

a large amount of electrolyte due to its bulkiness; thus the packing amount of manganese dioxide as a positive electrode material become smaller.

The present invention was completed in light of the above-mentioned circumstances, and it aims to furnish a dry-cell battery of excellent performance by using expanded graphite in part or wholly as a conductivity-enhancing additive in the positive electrode mix of a dry-cell battery, which uses manganese dioxide as a positive electrode material, zinc as a negative electrode material, and zinc chloride or ammonium chloride as an electrolyte to enhance the packing amount of manganese dioxide to improve the discharge utilization rate.

Expanded graphite, to be used as a part of or as the whole conductivity-enhancing additive in the present invention, is obtained by expanding the interlayers carbon planes in graphite; also, for instance, graphite can be oxidized by an oxidizing agent such as fuming nitric acid, concentrated sulfuric acid and concentrated nitric acid, chromic acid and concentrated sulfuric acid, perchloric acid, chromic acid and phosphoric acid, etc., to produce compounds in the carbon plane interlayers and heated directly or after washing with water at a temperature of greater than or equal to 100°C, for instance, 300°C, to evaporate the compounds produced in the interlayers to obtain expanded graphite.

When the expanded graphite is used as a conductivity-enhancing additive, the positive electrode mix can be molded even without adding an electrolyte of a larger amount than that in the case where acetylene black is used as the conductivity-enhancing additive. This is because the expanded graphite has a smaller electrical resistance than unexpanded graphite and is superior in

compressibility to acetylene black; moreover, the packing amount of the cathode mix is increased since its specific gravity is higher than acetylene black, and also the electrolyte sufficiently surrounds the manganese dioxide since the expanded graphite does not excessively absorb the electrolyte so that the discharge utilization rate is improved. Further, if the expanded graphite is used together with acetylene black it can solve the poor formability of acetylene black.

When only expanded graphite is used as a conductivity-enhancing additive, it is preferably used in an amount of 14-25 parts (parts by weight, hereinafter the same) per 100 parts of manganese dioxide, and when expanded graphite is used together with acetylene black, the conductivity-enhancing additive is preferably used in a total amount of 14-25 parts per 100 parts of manganese dioxide, in which the amount of expanded graphite in whole conductivity-enhancing additive is preferably greater than or equal to 10 wt%.

Next, the present invention is explained in further detail by application examples.

A positive electrode mix having a composition shown in Table I was packed into a foil-form separator placed on a carbon-zinc bonded electrode, encircled by a thermally shrinking polyvinyl chloride tube, and heated to thermally shrink the thermally shrinking polyvinyl chloride tube to adhere closely the positive electrode mix and the separator, the separator and the carbon-zinc bonded electrode, and those parts and the thermally shrinking polyvinyl chloride tube to obtain a battery unit; six battery units were laminated and metal sheets were contacted to the top and bottom edges of the laminate, compressed, and tied with a tape to form a block; this was dipped in a molten wax bath

to form a wax layer on the block surface and was encircled with a nonshrinkable polyvinyl chloride tube followed by attaching a lead and a terminal plate; it was then inserted into an outer cylinder, and the outer cylinder was clamped to obtain a 6F22-type laminar dry-cell battery by the ordinary method. Furthermore, the electrolyte used consisted of 3 wt% ammonium chloride, 27 wt% zinc chloride, and 70 wt% water.

The packing amount of the positive electrode mix for each composition in one battery unit and the discharge time of the laminar dry-cell battery in continuous discharge at 20°C and 600  $\Omega$  and also intermittent discharge (4 h/day) at 20°C and 600  $\Omega$  were determined, and the results are shown in Table I.

Table I

① 層状乾電池		A	B	C
② 組成	③ 二酸化マンガンの割合 (g)	40	40	40
	④ 膨張黒鉛の割合 (g)	9	2	—
	⑤ アセチレンブラックの割合 (g)	—	6	8
	⑥ 塩化アンモニウムの割合 (g)	7	7	7
	⑦ 電解液の割合 (g)	18	18	18
⑧ 1個あたりの電池台の充放電時間 (h)		24	22	21
⑨ 600 $\Omega$ 連続放電時間 (h)		14	13	11
⑩ 600 $\Omega$ 間欠放電時間 (h)		34	32	27

- Key: 1 Laminar dry-cell battery  
 2 Compositions  
 3 Manganese dioxide  
 4 Expanded graphite  
 5 Acetylene black  
 6 Ammonium chloride  
 7 Electrolyte

- 8     Packing amount of positive electrode mix in one battery unit(g)
- 9     Continuous discharge time at 600  $\Omega$  (h)
- 10    Intermittent discharge time at 600  $\Omega$  (h)

As shown in Table I, the packing amount of the positive electrode mix per one battery unit in the laminar dry-cell batteries A and B of the present invention is more than that in the conventional laminar dry-cell battery C, and thus the packing amount of manganese dioxide is also more than that in the conventional laminar dry-cell battery C. Further, as made clear from Table I, the discharge performance of the laminar dry-cell batteries A and B is superior to the conventional laminar dry-cell battery C. It is thought that the above results may be based on the increased discharge availability of manganese dioxide, as explained above, since the packing amount of manganese dioxide is increased, and expanded graphite, unlike acetylene black, does not excessively absorb the electrolyte so that the amount of electrolyte around the manganese dioxide is increased.

Furthermore, the present invention is applied not only to the laminar dry-cell batteries illustrated above but also to cylindrical dry-cell batteries and thin film type laminar dry-cell batteries.



Japanese Kokai Patent Application No. Sho 56[1981]-118267

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